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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for Producing a Metal-Plastic Film Composite Material, Metal-Plastic Film Composite Material Produced According to Said Process and Its Use for Producing Packaging Containers

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Production of a metal-plastic film laminate, the metal-plastic film laminate, and use thereof for manufacturing packaging containers

The present invention relates to a process for producing a metal-plastic film laminate by slot die extrusion of random polypropylene copolymer as a film which, on emerging from the slot die, is cooled by means of chill rolls and laminated onto at least one of the main surfaces of a metal sheet. The invention further relates to metal-plastic film laminates produced by the process of the invention and to the use of these laminates for manufacturing packaging containers.

A can or closure for use as a packaging material, in particular for foods, is manufactured from tinplate, chromated steel such as ECCS (electroliytic [sic] chromium-coated steel) and aluminum sheet after coating in panel or coil form. The coating acts as a protective layer, first protecting the metal from attack by the contents and the resulting corrosion and secondly preventing corrosion products of the metal affecting the contents. Of course, the contents must not be affected or impaired by the coating either, for example by constituents dissolved out of it, either in

the course of the sterilization of the contents carried out after filling or in the course of the subsequent storage of the packed goods, in particular foods.

Furthermore, the coatings must be such that, in the course of the further processing - forming, stamping, fringing, crimping and the like - of the coated sheets into cans or closures, they withstand the mechanical stresses which arise.

Moreover, high solvent emissions of the drying coating make it necessary to take precautions to minimize these emissions and the associated pollution.

An advantageous method for coating metal sheets which are to be used in particular for manufacturing food packages is film coating. For instance, DE-A-3 128 641 describes a process for producing laminates for food packages by heating the metal sheet and a thermoplastic resin film together with a carboxyl-containing polyolefin adhesive in between these layers to temperatures above the melting point of the adhesive and then cooling everything down together under pressure, thereby producing the metal-plastic laminate.

Furthermore, DE-A-2 912 023, GB-A-2 027 391 and EP-B-31 701 disclose laminates and food packaging containers, in particular bags, manufactured from these laminates.

Metal-plastic laminates are also used for example for stamping into valve plate carriers for aerosol cans.

The films for metal-plastic film laminates are customarily produced in an extrusion process in which the extruder is charged with thermoplastics in the form of powders or granules and the material is homogenized, plasticated, screw transported and forced through a shaping die in the extrusion head. A suitable way of producing polypropylene film is in particular the slot die extrusion process where the melt emerges hot from a wide slot in the die and then runs continuously directly over one or more chill rolls for cooling. The cooled film is edge trimmed, then usually corona-pretreated and subsequently wound up.

It is known that the chill roll temperature has an effect on the crystallinity and hence the optical and mechanical properties of the film in that low chill roll temperatures lead to films of relatively high transparency and toughness but of relatively lower stiffness and higher tendency to block. However, it is also known that the quenching of film can lead to stresses. Customary coolant feed temperatures are between 15°C and 30°C.

Conventional chill roll ranges produce polypropylene mono and coex films by cooling the chill rolls to temperatures above 20°C. With metal-laminated films produced in this way there is the problem that, after stamping, the laminates exhibit appreciable crazing. The crazing of metal-film laminates produced in this way is particularly pronounced in the case of plastic films based on random polypropylene copolymers.

Finally, EP-B-312 309 discloses a process for producing metal-polypropylene laminates in which a polypropylene film is laminated to a metal sheet and heated to a temperature above the melting point of polypropylene and the laminate is then cooled down to room temperature by flooding with a cold liquid. The advantages of the known process are that unevenness in the coating is suppressed. However, there is a problem with the process known from EP-B-312 309 in that the laminates produced by it are not completely free of crazing.

It is an object of the present invention to develop a process for producing metal-plastic laminates based on polypropylene random copolymers which are free of crazing and suitable for manufacturing packaging containers, in particular for the food sector. The metal-plastic laminates shall have excellent barrier properties - low optical transmissivity, low water vapor permeability and generally low gas permeability. The laminates shall be suitable in particular for packaging foods and snacks.

This object is surprisingly achieved by a process for producing a metal-plastic film laminate by slot die extrusion of random polypropylene copolymer as a film which, on emerging from the slot die, is cooled by means of chill rolls and laminated onto a metal sheet, which comprises quenching the polypropylene copolymer to temperatures between 0°C and 15°C directly on emerging from the slot die of the extruder and,

after the plastic film has been laminated to the metal sheet by means of a solvent-containing or aqueous adhesive, cooling the resulting metal-plastic film laminate to temperatures of 0°C to 25°C when the laminating of the film onto the metal sheet has taken place at temperatures above the melting point of the polypropylene copolymer of the plastic film, or, after the plastic film has been laminated onto the metal sheet by means of a coextruded adhesion promoter, cooling the resulting metal-plastic film laminate to temperatures of 0°C to 25°C.

Preferably the extruded polypropylene copolymer is quenched to temperatures within the range from 5°C to 10°C directly after emerging from the slot die of the extruder.

It is surprising and was unforeseeable that, in the process of the invention, no stresses arise in the films and the films or metal-plastic film laminates are free of crazing after stamping.

The present process utilizes for example the following coolants for cooling the roll downstream of the slot die extruder: water, water-cattle salt mixtures, coolants based for example on ethylene glycol, for example the commercially available coolant Glysantin® (BASF AG).

The coolant feed temperatures are within the range from 0°C to 15°C. Owing to the thickness of the extruded films, usually within the range from 10 to 250 μm, and the customary high production speeds, the

polypropylene random copolymer films emerging from the slot die are therefore brought immediately to temperatures between 0°C and 15°C.

The random polypropylene copolymers used in the process of the invention are random copolymers comprising 92 to 99% by weight of propylene and 1 to 8% by weight of comonomers, each percentage being based on the total weight of the monomer composition. Suitable comonomers are C_2-C_{12}-, preferably C_2-C_6-α-monoolefins, for example ethene, 1-butene, 4-methyl-1-pentene, 1-hexene, n-1-octene, n-1-decene and n-1-dodecene. Polypropylene copolymers of this type are well known and commercially available in a multiplicity of grades, for example under the name Novolen (BASF AG). The random copolymers are preparable for example in the process described in DE-A-3 730 022. They have a melt flow index MFI 230°C/2.16 kp within the range from 4 to 12 g/10 min (measured in accordance with DIN 53 735).

The films obtainable from the polypropylene random copolymers are used as the thermoplastic top layer of the metal-plastic film laminate. Of course, laminate films obtained by coextruding of at least two different resins can also be used as the top layer of the laminate. For instance, the random polypropylene copolymers can be for example mixed and coextruded with other random copolymers or with polypropylene homopolymers or else with further polyolefins, polyamides, polyesters, polyvinyl chloride, polyvinylidene chloride and polycarbonates. The preferred

thermoplastic film, which constitutes the innermost layer (i.e. the layer in contact with the contents) of the metal-plastic film laminate, however, comprises polypropylene random copolymers only.

The particularly preferred plastic film base material for the process of the invention comprises random polypropylene copolymers obtained by random copolymerization of 1 to 4% by weight of ethylene and 99 to 96% by weight of propylene, each percentage being based on the total weight of the monomer composition. The metal-plastic film laminates produced by the process of the invention using these copolymers are completely free of any tinplate [sic] after stamping.

The thermoplastic polypropylene copolymer films usually additionally comprise additives, for example internal and external lubricants, antiblocking agents, stabilizers, antioxidants, pigments, crystallization aids and the like. These additives are used in the amounts necessary for synthesis, processing, fabrication and application, in the form of coarse powders, fine powders, granules or a concentrate incorporated directly in the polymer. Details of the amounts customarily used and examples of suitable additives may be found for example in Gächter-Müller, Kunststoff-additive, Carl-Hanser Verlag.

The process of the invention can utilize mono or multi-layer films which are laminated onto the metal sheet by means of a solvent-containing or aqueous adhesive. In addition, however, it is also possible to

coextrude the polypropylene plastic together with an adhesion promoter and to laminate the resulting coexfilm onto the metal sheet.

The polymers used in the process of the invention as adhesive or as adhesion promoter layer can be both copolymers, terpolymers, graft copolymers and ionomers, provided they contain carboxyl or anhydride groups or groups which are hydrolyzable to carboxyl groups and that the melt flow index of the polymer, measured at 190°C under a load of 2.16 kg, is between 0.1 and 30 g/10 min, preferably between 0.2 and 25 g/min and particularly preferably between 0.5 and 20 g/10 min.

Suitable co- and terpolymers are preparable by copolymerization of ethylene with α,β-unsaturated carboxylic acids such as, for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid and fumaric acid, the corresponding anhydrides or the corresponding esters or monoesters having from 1 to 8 carbon atoms in the alcohol moiety, such as, for example, the methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl and 2-ethylhexyl esters of the acids mentioned. It is also possible to use the corresponding salts of the carboxylic acids mentioned, for example the sodium, potassium, lithium, magnesium, calcium, zinc and ammonium salts. Preference is given to using the carboxylic acids and their anhydrides.

Further monomers that are copolymerizable with ethylene and the unsaturated carbonyl compounds can be used in the copolymerization. Examples are alpha olefins having 3 to 10 carbon atoms, vinyl acetate and vinyl propionate.

The amounts of the monomers used are chosen in such a way that the resulting polymer has a carboxyl group content of 0.1 to 30% by weight, preferably 2 to 20% by weight.

Suitable graft copolymers are preparable by grafting at least one polymer of the group of the polyolefins with up to 10% by weight, preferably up to 5% by weight, based on the total weight of the monomers, of at least one monomer from the group of the α,β-unsaturated carboxylic acids, their anhydrides, their esters or salts in the presence or absence of peroxides. DE-A-3 800 307 and DE-A-3 639 564 describe suitable adhesion promoters based on graft copolymers and methods for preparing them.

The ionomers used as adhesion promoter layer are preparable by the above-described copolymerization of ethylene and optionally further monomers with salts of α,β-unsaturated carboxylic acids or by partial neutralization of the above-described carboxyl-containing co-, ter- and graft polymers with salts, oxides and hydroxides of sodium, potassium, lithium, magnesium, calcium, zinc and ammonium. The neutralization can be carried out in the melt or in solution. The amount of basic compound is chosen in such a way

that the degree of neutralization of the polymer is between 0.1 and 99%, preferably between 0.1 and 75%, and very particularly preferably between 0.1 and 40%.

The adhesion promoter which is coextruded with the polypropylene random copolymer is particularly preferably a polypropylene which has been polar modified, preferably grafted with maleic anhydride.

The contemplated adhesives are applied from solutions or dispersions in water or organic solvents. The solutions or dispersions generally have an adhesive content of 5 to 60% by weight. Particularly suitable adhesives comprise thermoplastic resins, such as cellulose esters, cellulose ethers, acrylic esters, polyamides, polyurethanes and polyesters, thermosetting resins, such as epoxy resins, urea-formaldehyde resins, phenol-formaldehyde resins and melamine-formaldehyde resins. The preferred adhesive is a solvent-containing two-component polyurethane adhesive.

Suitable metal sheets are sheets from 0.04 to 1 mm in thickness made of blackplate, tinplate, aluminum and various iron alloys which may have been optionally provided with a passivating layer based on nickel, chromium and zinc compounds.

In the process of the invention, the polypropylene film is laminated onto the metal sheet, the film being adhered to the metal using either a solvent-containing or aqueous adhesive or a coextruded adhesion promoter. The production of metal-plastic film

laminates by means of adhesion promoters is a generally known process.

It comprises first coextruding the thermoplastic polymer and the adhesion promoter. The metal sheet is then covered with the coextruded film in such a way that the adhesion promoter layer of the coexfilm touches the metal surface. The polypropylene top layer-adhesion promoter-metal laminate is produced either by means of a temperature controllable press or in the nip of a pair of squeeze rolls or of a calender by means of temperature controllable rolls by application of pressure and heat. The pressure and temperature have to be chosen in such a way that the adhesion promoter enters a firm and stable bond with the metal foil or sheet and that, on the other hand, the thermoplastic top layer should ideally not melt. Afterwards the laminate is cooled down to temperatures of 0°C to 25°C. This is preferably done by passing the laminate through a cooling bath. However, it is also possible to cool down the laminates by means of an air blower.

If a solvent-containing or aqueous adhesive is used, the metal-plastic film laminate is produced by applying the adhesive to a metal sheet, heating, and laminating the plastic film onto the metal sheet by application of pressure and heat.

Bonding propylene film to metal by means of an aqueous or solvent-containing adhesive can be carried out on slow-running machines, i.e. at laminating speeds of 5 to 60 m/min, at temperatures below 130°C. If the

laminating of the plastic film to the metal sheet is carried out at temperatures below 130°C, it is in general not necessary to cool the metal-plastic film laminate obtained, since no melting of the polypropylene plastic film takes place. According to the invention, however, if the film has been laminated to the metal sheet at temperatures above the melting point of the polypropylene plastic film, i.e. in general above 130°C, the resulting metal-plastic film laminate is cooled down to temperatures of 0°C to 25°C. High speed machinery is run at bonding or laminating speeds between 60 and 150 m/min, so that elevated temperatures of about 180°C to 220°C are necessary for producing the metal-plastic film laminates. In this case the invention provides that, after the film has been laminated to the metal sheet and the laminate heated, it be quenched to temperatures of 0°C to 25°C. The laminate is quenched for example by passing it through a cooling bath.

If the film has been laminated to the metal sheet at temperatures above the melting point of the polypropylene of the plastic film, the laminate is cooled down to temperatures of 0°C to 25°C.

The quenching of the laminates can take place for example in a water or ice-water bath through which the laminates pass. It is also possible, as mentioned earlier, to cool down the metal-plastic laminates by means of an air blower.

The coating of the metal sheet, i.e. the thermoplastic lamination film, generally has a total dry film thickness of less than 500 μm, preferably 10 to 200 μm. In this the thickness of the adhesion promoter layer or of the adhesive layer accounts for between 0.5 and 100 μm. The top layer accordingly has a thickness of between 10 and 499.5 μm.

For the purposes of the present invention metal-plastic film laminates also include laminates in which the metal sheet has been coated with a polypropylene film on both sides.

The invention likewise concerns the metal-plastic film laminates produced by the process of the invention. These laminates are stamped for example to form cans, jar closures, crown cork or valve plate carriers for aerosol cans. The laminates are notable in particular for their absence of crazing. If, for comparison, the polypropylene copolymers emerging from the slot die of the extruder are not cooled down to temperatures of 0°C to 15°C and if, after the films have been laminated to the metal sheet at temperatures of above 130°C, there is no cooling down to temperatures of from 5°C to 25°C, films of the metal-plastic laminates show distinct crazing.

The metal-plastic film laminates of the invention are used for manufacturing packaging containers, in particular for manufacturing bottoms and lids of cans, valve plates of aerosol cans, and closures. The manufacturing methods employed are conventional (cf.

for example VR-INTERPACK 1969, pages 600-606: W. Panknin, A. Breuer, M. Sodeik, "Abstreckziehen als Verfahren zum Herstellen von Dosen aus Weißblech"; SHEET METAL INDUSTRIES, August 1976: W. Panknin, CH. Schneider, M. Sodeik, "Plastic Deformation of Tinplate in Can Manufacturing"; Verpackungs-Rundschau, No. 4/1971, pages 450-458: M. Sodeik, I. Siewert, "Die nahtlose Dose aus Weißblech"; Verpackungs-Rundschau, No. 11/1975, pages 1402 to 1407: M. Sodeik, K. Haaβ, I. Siewert, "Herstellen von Dosen aus Weißblech durch Tiefziehen"; Arbeitsmappe für den Verpackungspraktiker, Metalle, Teil II, Gruppe 2, Weißblech, Lfd.-No. 220.042 to 220.048 in neue Verpackung 12/87, page B 244 to B 246 and neue Verpackung 1/88, pages B 247 to B 250).

For further details reference is therefore made to the literature.

The invention will now be illustrated by examples:

Example 1:

A commercially available polypropylene copolymer (trade name Novolen® 3225 MCX from BASF AG) is coextruded with a commercially available adhesion promoter based on maleic anhydride-grafted polypropylene (trade name Modic P 301 from Mitsubishi Chemical Ind.) on a slot die extrusion range.

Both the materials are used in granule form. The main extruder is a 90 mm ø 25 D extruder from Barmag, and the coextruder is a 45 mm ø 25 D extruder from Schwabethan. The bushing of the main extruder is

smooth, while that of the coextruder has grooves. The melt of the polypropylene Novolen 3225 MCX is at 260°C, while that of the adhesion promoter is at 232°C. The melt pressure of the Novolen is 60 bar and that of the adhesion promoter 35 bar. The zone temperatures of the main extruder are between 210°C and 235°C and those of the coextruder between 180°C and 210°C. The water-cooled chill roll is at 10°C. The thickness of the polypropylene base film is 40 µm and that of the adhesion promoter film 10 µm. An air knife is run at 60 mbar.

Using temperature controllable rolls at 30°C, the coextruded film is laminated onto a hot metal sheet at 170°C. The laminate obtained is then passed through a water bath at 16°C.

The metal-plastic film laminate is stamped. It is free of crazing.

Example 2:

Example 1 is repeated with the difference that, in the slot die extrusion, the coextruded film emerging from the slot die is cooled down to 20°C. The metal-plastic laminate obtained exhibits crazing on stamping.

Example 3:

The polypropylene copolymer obtainable under the trade name Novolen® 3225 MCX (BASF AG) is extruded on a slot die extrusion range from Barmag (90 mm ø 25 D). The polypropylene is used in granule form. The bushing of the extruder is smooth. The melt of the polypropylene plastic is at 260°C and its

pressure is 60 bar. The zone temperatures of the extruder are between 210°C and 235°C. On emerging from the slot die the film is cooled down to 8°C with the aid of a water-cooled chill roll. The thickness of the polypropylene film is 80 µm. An air knife is operated at 60 mbar.

A commercial solvent-containing two-component polyurethane adhesive is applied to a metal sheet by roller coating in a wet film thickness of 6 to 8 µm and passed through an oven at about 180°C. The metal foil to which the adhesive has been applied is laminated with the polypropylene film at a temperature of 110°C. The metal-plastic film laminate obtained is stamped. It is completely free of crazing.

Example 4:

Example 3 is repeated with the difference that the laminating of the polypropylene film onto the metal sheet is carried out at a temperature of 180°C. The resulting laminate shows crazing on stamping.

Example 5:

Example 3 is repeated with the difference that the laminating of the polypropylene film onto the metal sheet is carried out at a temperature of 180°C. The resulting metal-plastic laminate is afterwards passed through a water bath at a temperature of 10°C. The laminate obtained is free of crazing on stamping.

Claims

1. A process for producing a metal-plastic film laminate by slot die extrusion of random polypropylene copolymer as a film which, on emerging from the slot die, is cooled by means of chill rolls and laminated onto at least one of the main surfaces of a metal sheet, which comprises quenching the polypropylene copolymer to temperatures between 0°C and 15°C directly on emerging from the slot die of the extruder and, after the plastic film has been laminated to the metal sheet by means of a solvent-containing or aqueous adhesive, cooling the resulting metal-plastic film laminate to temperatures onto 0°C to 25°C when the laminating of the film onto the metal sheet has taken place at temperatures above the melting point of the polypropylene copolymer of the plastic film, or, after the plastic film has been laminated onto the metal sheet by means of a coextruded adhesion promoter, cooling the resulting metal-plastic film laminate to temperatures of 0°C to 25°C.

2. The process of claim 1, wherein the polypropylene copolymer is quenched to temperatures within the range from 5°C to 10°C directly and [sic] emerging from the slot die of the extruder.

3. The process of claim 1 or 2, wherein the polypropylene plastic film is a mono film which is laminated onto the metal sheet by means of a solvent-containing polyurethane adhesive.

4. The process of claim 1 or 2, wherein the polypropylene plastic is coextruded together with an adhesion promoter comprising polar modified polypropylene and the coex film is then laminated onto the metal sheet.

5. The process of any one of claims 1 to 4, wherein the random polypropylene copolymer is obtainable from 1 to 4% by weight of ethylene and 99 to 96% by weight of propylene, based on the total weight of the monomer composition.

6. A metal-plastic film laminate produced as claimed in one or more of claims 1 to 5.

7. The use of a metal-plastic film laminate of claim 6 for manufacturing packaging containers.

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Abstract

Production of a metal-plastic film laminate, the metal-plastic film laminate, and use thereof for manufacturing packaging containers

The present invention relates to a process for producing a metal-plastic film laminate by slot die extrusion of random polypropylene copolymer as a film which, on emerging from the slot die, is cooled by means of chill rolls and laminated onto at least one of the main surfaces of a metal sheet, which comprises quenching the polypropylene copolymer to temperatures between 0°C and 15°C directly on emerging from the slot die of the extruder and, after the plastic film has been laminated to the metal sheet by means of a solvent-containing or aqueous adhesive, cooling the resulting metal-plastic film laminate to temperatures of 0°C to 25°C when the laminating of the film of the metal sheet has taken place at temperatures above the melting point of the polypropylene copolymer of the plastic film, or, after the plastic film has been laminated onto the metal sheet by means of a coextruded adhesion promoter, cooling the resulting metal-plastic film laminate to temperatures of 0°C to 25°C.

The present invention further relates to the metal-film laminate produced by the process of the invention and to its use for manufacturing packaging containers.